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First Principle Calculation of Electronic Structure of $Ca_2Co_2O_5$ Thermoelectric Compound Oxide

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Abstract

First principle calculations are employed to investigate the thermoelectric $Ca_2Co_2O_5$ with regard to its geometry and ground state electronic structure. The P-type thermoelectric $Ca_2Co_2O_5$ is found to be more stable via total energy minimization calculations; the calculated energy band structure reveals its band overlap. The valence band in the $Ca_2Co_2O_5$ is composed only of Co 3d and O 2p orbitals, the bands that have the Co 3d component must be enhanced at the Co 2p–3d resonance and heavy carriers in valence bands that should favour high thermoelectric properties. The Co-3d and O-2p orbitals are responsible for energy bands near Fermi level and they contribute to electronic property.

Keywords: first principle calculation; thermoelectric materials of $Ca_2Co_2O_5$; electronic structure

1. Introduction

Recently, thermoelectric materials are renewed interesting as clean energy conversion into electric energy [1]. The thermoelectric material is usually evaluated by the dimensionless figure of merit $ZT = S^2\rho T/\kappa$, where S, ρ, T and κ are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. Good thermoelectric materials should simultaneously exhibit lowest κ and highest S and ρ [2]. We are focused in oxide thermoelectric materials because low or non toxicity and friendly environment. Many oxides have demonstrated good thermoelectric properties such as $NaCo_2O_4$ [3-5] compounds and Ca-Co-O system compounds [6-7], etc, which are comparable or better

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than values reported for Bi_2Te_3. Moreover, Miyazaki [7] reported neutron scattering indicated that $[Ca_2CoO_3]_{0.62}CoO_2$ compounds consisted of two structures which were $[Ca_2CoO_3]$ and $[CoO_2]$, respectively. Lattice parameters a, c and angle ß of the two structures are the same, i.e. a = 4.8339 Å, c = 10.8436 Å and ß = 98.14º. However, b_1 is 2.82 Å for $[CoO_2]$ and b_2 is 4.56 Å for $[Ca_2CoO_3]$. In 2005, Y. Zhang [8] prepared calcium cobalt oxides ($Ca_2Co_2O_5$) compounds using spark plasma sintering and achieved Seebeck coefficient of ~153 μVK^{-1}. In addition, three years after, layered $Ca_2Co_2O_5$ were reported to possess fairly good TE performances [7, 9]. However, there have been only a few reports on the electronic structures of $Ca_2Co_2O_5$ especially with the energy level and density of state etc.

In this work, we are designed the geometric crystal structures and calculated the band structures and density of states of $Ca_2Co_2O_5$ by first principle calculation method.

2. Computational detail

In the first principle calculation has used data of $Ca_2Co_2O_5$ compounds such as space group 8 (*Cm*), the lattice parameters a = 4.8339 Å, b = 2.8238 Å, c = 10.8346 Å and β = 98.14˚ and b_2 = 4.5582 Å [6-7]. The ultra-soft pseudo-potential plane wave method and generalized gradient approximations (GGA) based on density functional theory (DFT) is performed using the Cambridge serial total energy package (CASTEP) method [10]. The Pseudo atomic calculation for O ($2s^2$, $2p^4$), Ca ($3s^2$ $3p^6$ $4s^2$) and Co ($3d^7$ $4s^2$) is performed. The electron-ion interaction is described by a Vanderbilt's ultrasoft pseudo-potentials. The exchange correlation interaction energy is described using Perdew Burke Ernzerh (BPE) functional within GGA framework. In the total energy calculations, integrations over the Brillouin zone are performed for the unit cell. The valence electronic wave functions are expanded in a plane-wave basis set up to an energy cutoff of 300 eV. In the electronic structure calculation, the Monkhorst-pack grid 4×7×2 is used for k-point sampling. Then the electronic structure is analyzed in terms of the band structure and density of states (DOS).

3. Results and discussion

The geometric crystal structures of $Ca_2Co_2O_5$ compounds are showed in Fig. 1.

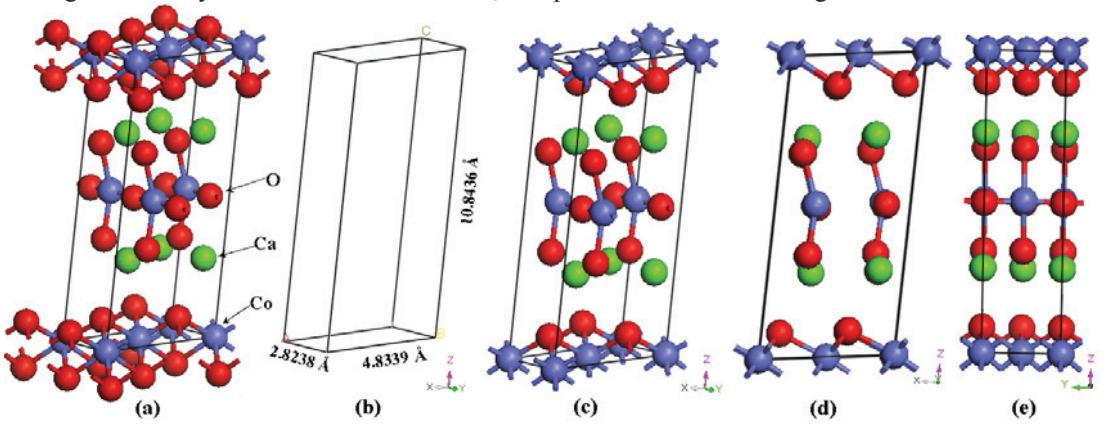

Fig. 1. (a) crystal structure of $Ca_2Co_2O_5$, (b) unit cell, (c), (d) and (e) the rail atomic numbers in unit cell of (111), (010) and (100) planes, respectively

Figure 1 (a) and (b) show the default crystal structures of $Ca_2Co_2O_5$ compounds and unit cell shows lattice parameters a, b and c values. Considering crystal structures of $Ca_2Co_2O_5$ compounds were

composed of CoO_2 layers on top and bottom of unit cell side which outer CdI_2 structure type together with triangular lattices consist of edge-sharing $CozO_6$ octahedrons [2, 6] and Ca_2CoO_3 layer on halve of unit cell at a distorted rock-salt structure type with lattice parameter constant of 4.56 Å [2, 6-7]. However, the Ca_2CoO_3 layer is rock-salt structure which not showed and considered which in this calculation used unit cell of CoO_2 is essentially. In unit cell of $Ca_2Co_2O_5$ compounds are show in Fig. 1 (c)-(e). In Fig. 1 (c)-(e), the ratios of atom in unit cell consist of Ca = 4 atoms, Co = 4 atoms and O = 10 atoms, which the rail atomic numbers in unit cell of $Ca_2Co_2O_5$ structures show (010) and (100) planes. Therefore, Fig. 1 (c)-(e), the atomic ratio was confirmed the $Ca_2Co_2O_5$ compounds within the chemical composition. The calculated band structures comparing with the total density of states of are show in Fig. 2. (a) and (b), respectively, and the partial density of states are show in Fig. 3.

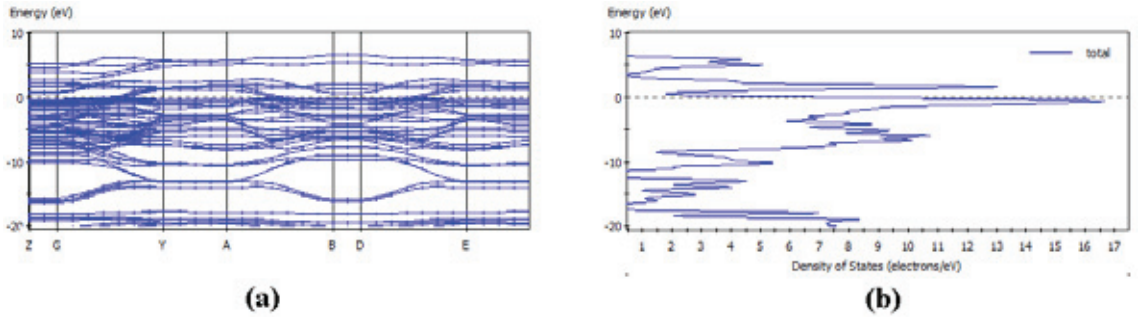

Fig. 2. (a) band structure and (b) total density of states of $Ca_2Co_2O_5$ in energy range of -20 eV to 10 eV; the horizontal dotted lines denote the Fermi level E_F

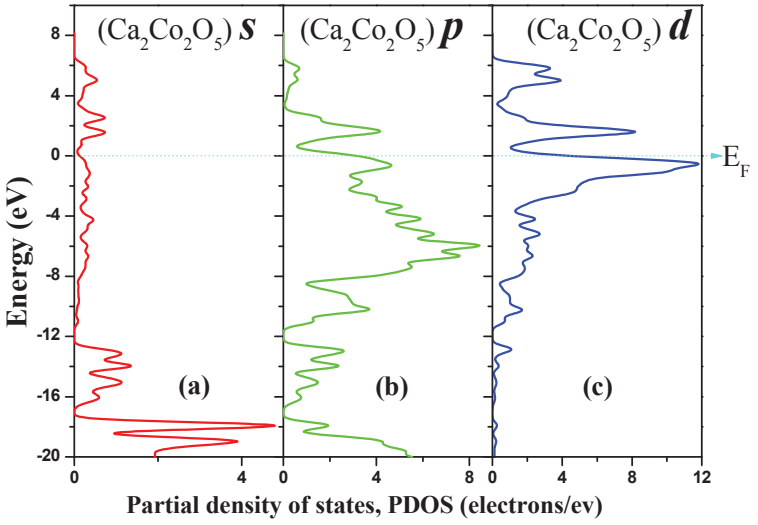

Fig. 3. Partial density of states of $Ca_2Co_2O_5$ compounds show of (a) s orbital, (b) p orbital and (c) d orbital in energy range of 20 eV to 10 eV, respectively

In Fig. 2 (a), the band structures of $Ca_2Co_2O_5$ compounds are shown with band overlapping between O 2p and Co 3d orbitals, a metallic behaviors and in agreement with highest density of state under Fermi level (fixed at 0 eV) as shown in Fig. 2 (b). The band overlap obtained by the partial density of states of $Ca_2Co_2O_5$ compounds as shown in Fig. 3 composed of (a) s-orbital, (b) p-orbital and (c) d-orbital in energy range of -20 eV to 10 eV, respectively. The highest density of state under Fermi level shown is of P-type thermoelectric materials [12]. The effect of metallic behavior is high electrical conductivity, of $Ca_2Co_2O_5$ compounds in agreement with literature data [8].

4. Conclusion

The geometry and ground state electronic structure of $Ca_2Co_2O_5$ compounds can be simulated by first principle calculation of CASTEP. The electronic structure was analyzed in terms of the crystal structures, band structure and density of states. The atomic ratio confirmed that the $Ca_2Co_2O_5$ compounds are within the chemical composition. The band structures show band overlapping between O 2p and Co 3d orbitals in agreement with highest density of state at just under Fermi level. The investigation on thermoelectric properties show the $Ca_2Co_2O_5$ compounds has metallic behaviors and exhibit P-type thermoelectric materials with highest density of state under Fermi level.

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